Semi-Annual Status Report For NAG5-738

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APPLICATION AND DEVELOPMENT OF THE

PARTIAL DIFFERENTIAL EQUATION METHOD IN

ELECTRON-MOLECULE SCATTERING

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PROGRESS

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The 15 state vibrational close-coupling calculation for $e^- + N_2$ within the hybrid theory has been completed. The $K - matrices$ are stored in the HSM file system at NASA-Goddard. I am in the process of retrieving them so as to calculate differential cross sections at various energies corresponding to the possible vibrational excitation processes.

An investigation of the accuracy of the existing PDE code, which was written using a three point difference scheme for first derivatives, has been conducted. This was done in the context of the necessity for calculating continuum wavefunctions when it is required to enforce orthogonality constraints between the continuum orbital and bound orbitals of the same symmetry. To understand the context of this observation, I now discuss various aspects of the PDE method.

I. Extension of the PDE Method to
Electron-Molecular Ion Scattering

(A) Static Exchange Approximation

The basic equations to be solved are illustrated by the static exchange equation

$$[\hat{\nabla}^2 + k^2]F(\vec{r}) = 2V(\vec{r})F(\vec{r})$$
$$-2\sum_{i=1}^{N_E} \hat{W}_{\alpha_i}(\vec{r})\Phi_{\alpha_i}(\vec{r}). \tag{1}$$

This is the most simple but reasonably realistic equation that is encountered in electron-molecule scattering. F represents the Continuum orbital; $\vec{r}$ represents the continuum electron position vector; $\hat{W}$, the exchange kernel, is given by

$$\hat{W}_{\alpha_i}(\vec{r}) = \int d\vec{x} \ \Phi_{\alpha_i}(\vec{x})\frac{1}{|\vec{r} - \vec{x}|}F(\vec{x}). \tag{2}$$

Φ is a bound orbital of the target molecule. Realize that

$$\hat{\nabla}^2(|\vec{r} - \vec{x}|^{-1}) = -4\pi\delta(\vec{r} - \vec{x}). \tag{3}$$

Then, two coupled equations, which must be solved simultaneously, are then obtained

$$[\hat{\nabla}^2 + k^2]F(\vec{r}) = 2V(\vec{r})F(\vec{r})$$
$$-2\sum_{i=1}^{N_E} \Phi_{\alpha_i}(\vec{r})\hat{W}_{\alpha_i}(\vec{r}) \tag{4}$$

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$$\hat{\nabla}^2 \hat{W}_{\alpha_i}(\vec{r}) = -4\pi \Phi^*_{\alpha_i}(\vec{r}) F(\vec{r}) \qquad (5)$$

$\hat{W}$ plays the part of a pseudo–continuum orbital. It has the value of zero on the large r boundary. There are as many inhomogeneous equations like (5) as there are bound molecular orbitals.

Eqs. (4) and (5) are elliptic PDEs. They are solved by applying a finite difference approximation to $\hat{\nabla}^2$ to produce

$$\underline{A}\underline{F} = \underline{B} \qquad (6)$$

$\underline{A}$ is the block tridiagonal coefficient matrix, $\underline{F}$ is the solution vector, and $\underline{B}$ is the boundary vector.

At the $r = \rho$ boundary, the partial-wave solutions are extracted by expanding the PDE solution, for each symmetry m, in partial waves.

$$F^m(\vec{r}) = \sum_{l_i} a_{l_i} \sum_{l_j} f^m_{l_i l_j}(r) Y^m_{l_j}(\theta, \phi) \qquad (7)$$

The $a's$ are arbitrary amplitudes. The $f's$ have the form

$$f_{l_i l_j}(r) = S_{l_i}(r) P_{l_i l_j}(r) + C_{l_i}(r) Q_{l_i l_j}(r) \qquad (8)$$

The S and C are spherical Bessel functions if the target is neutral and Coulomb functions if the target is charged. The value $r = \rho$ is determined by the range of the exchange contribution. The P and Q can be combined into a multidimensional vector I and propagated to an approximate ∞.

$$\underline{I}(r_f) = \underline{T}(r_f)\underline{I}(r_i) \qquad (9)$$

$\underline{T}$ is the propagator. The reaction matrix is then computed by

$$\underline{K} = \underline{Q}\underline{P}^{-1} \qquad (10)$$

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(B) Extension To Charged Or Open Shell Targets

We have generalized the PDE method to treat charged and open shell targets and multichannels in the fixed nuclei approximation (FNA). This means that the S and C are Coulomb funtions for charged targets. To treat general open shell targets, we must expand

$$\Psi^{(}m) = \hat{A} \sum_{i=1}^{n_T} \Phi_i(1, \ldots, N) F_{ij}^m(N+1)$$
$$+ \sum_{a=1}^{n_c} \beta_i(1, \ldots, N+1) C_{a,j}$$

(11)

Here, the β's are correlation terms. This results in the equation

$$[\hat{\nabla}^2 + k_i^2] F_{ik}^m(\vec{r}) = 2 \sum_{j=1}^{n_t} [V_{ij}(\vec{r}) + \hat{W}_{ij}(\vec{r})] F_{jk}^m(\vec{r})$$
$$+ 2 \sum_{a=1}^{n_c} U_{ia}(\vec{r}) C_{ak}$$

(12)

Note that the Lagrange multipliers are not needed since the orthogonality is enforced by the specification of the value of 0 on the $r = \rho$ boundary in the B vector. They can be put in as an internal check (which we do). The C in (11) satisfies

$$\sum_{b=1}^{n_c} \Omega_{ab} C_{bj} + \sum_{i=1}^{n_t} \langle U_{ia} | F_{ij}^m \rangle = 0$$

(12)

where $a = (1, \ldots, n_c)$ and $j = (1, \ldots, n_t)$, and j is fixed. U and Ω are defined by

$$U_{ia}(\vec{r}) = \sum_{\alpha_i=1}^{n_c} \langle \Phi_{\alpha_i} | \hat{H}_{N+1} - E | \beta_a \rangle$$

(13)

$$\Omega_{ab} = \langle \beta_a | \hat{H}_{N+1} - E | \beta_b \rangle$$

(14)

We might note that the correlation terms are of two types: (1) those that are required to relax orthogonality and ; (2) those that are required to produce projectile-target correlation (both short and long range).

Eqs. (12) are solved in the standard manner. In this procedure, F is expanded as (drop the m symmetry notation)

$$F_{ik}(\vec{r}) = F_{ik}^{(0)}(\vec{r}) + \sum_{a=1}^{n_c} F_i^{(a)}(\vec{r}) C_{ak}$$

(15)

Then the actual equations to be solved are

$$[\hat{\nabla}^2 + k_i^2]F_{ik}^{(0)}(\vec{r}) = 2\sum_{j=1}^{n_t}[V_{ij}(\vec{r}) + \hat{W}_{ij}^{(0)}(\vec{r})]F_{jk}^{(0)}(\vec{r}) \tag{16}$$

$$[\hat{\nabla}^2 + k_i^2]F_i^{(a)}(\vec{r}) = 2\sum_{j=1}^{n_t}[V_{ij}(\vec{r}) + \hat{W}_{ij}^{(a)}(\vec{r})]F_j^{(a)}(\vec{r}) \\ + 2U_{ia}(\vec{r}) \tag{17}$$

The W's are here defined by

$$\hat{\nabla}^2\hat{W}_{ij}^{(0)}(\vec{r}) = -4\pi\sum_{k=1}^{n_t}\overline{\Phi}_{ik}^*(\vec{r})F_{kj}^{(0)}(\vec{r}) \tag{18}$$

$$\hat{\nabla}^2\hat{W}_{ij}^{(a)}(\vec{r}) = -4\pi\sum_{k=1}^{n_t}\overline{\Phi}_{ik}^*(\vec{r})F_k^{(a)}(\vec{r}) \tag{19}$$

Thus the formalism is similar to that of the Linear Algebraic Method of Schneider and Collins. The primary difference is that we are solving PDE's instead of ordinary differential equations.

Each of the Eqs. (18) and (19) may be solved independly on different processors and then combined after solution. For those correlation terms included in Eq. (12) that are not required to relax orthogonality, an optical potential will be constructed in the manner of Schneider and Collins.

II. PDE Vibrational Close-Coupling

To treat vibrational excitation within the close-coupling formalism, consider the time-independent Schrödinger equation with the vibrational Hamiltonian and explicit dependence on the internuclear distance R included

$$[\hat{\nabla}^2 - 2\hat{H}_{vib} + k^2]F(\vec{r}, R) = 2V(\vec{r}, R)F(\vec{r}, R) \\ -2\sum_{i=1}^{N_E}\hat{W}_{\alpha_i}(\vec{r}, R)\Phi_{\alpha_i}(\vec{r}, R). \tag{20}$$

where

$$\hat{H}_{vib}\phi_v(R) = E_v\phi_v(R) \tag{21}$$

The solution is obtained by expanding as

$$F(\vec{r}, R) = \sum_{v=0}^{v_{max}}F_v(\vec{r})\phi_v(R) \tag{22}$$

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$$\hat{W}_{\alpha_i}(\vec{r}, R) = \sum_{v=0}^{v_{max}} \hat{W}_v^{(\alpha_i)}(\vec{r})\phi_v(R) \qquad (23)$$

Then, the generalizations for vibrational close-coupling are obtained

$$[\hat{\nabla}^2 + k_v^2]F_v(\vec{r}) = 2\sum_{v'} V_{vv'}(\vec{r})F_{v'}(\vec{r})$$

$$-2\sum_{v'}\sum_{i=1}^{N_E} \Phi_{vv'}^{(\alpha_i)}(\vec{r})\hat{W}_{v'}^{(\alpha_i)}(\vec{r}) \qquad (24)$$

$$\hat{\nabla}^2 \hat{W}_v^{(\alpha_i)}(\vec{r}) = -4\pi \sum_{v'} \Phi_{vv'}^{(\alpha_i)*}(\vec{r})F_{v'}(\vec{r}) \qquad (25)$$

Now consider the extension of the PDE method to a discretized internuclear separation. The following derivation is attributable to Dr. Aaron Temkin.

III. 3D PDE: Discretized Internuclear Separation

(A) Reduction of Scattering Equation to 3D

We specialize to $e - N_2$.

$$\Psi = \hat{A}[\psi(\vec{r}, R)\Phi_{N_2}(\vec{x}_1, \ldots, \vec{x}_{14})] \qquad (26)$$

Where ψ is the scattering orbital. Note:

$$R = |\vec{R}_A - \vec{R}_B| \qquad (27)$$

We will employ a local exchange potential $\Rightarrow$ neglect $\hat{A}$. Substitution of (26) into the Schrödinger equation and premultiplication by $\langle\Phi_{N_2}^*|$ gives (use Rydberg units)

$$\{ -\hat{\nabla}_{\vec{r}}^2 - \frac{1}{(M_A/m_e)}\hat{\nabla}_{\vec{R}_A}^2 - \frac{1}{(M_B/m_e)}\hat{\nabla}_{\vec{R}_B}^2 $$

$$+ \langle\Phi_{N_2}^*|[V_{e-N_2} + H_{N_2}]|\Phi_{N_2}\rangle - E\}\psi(\vec{r}, R) = 0 \qquad (28)$$

Decompose the kinetic energies of the nuclei into relative and c.m. coordinates and neglect the latter $\Rightarrow$

$$\frac{1}{M_A}\hat{\nabla}_{\vec{R}_A}^2 + \frac{1}{M_B}\hat{\nabla}_{\vec{R}_B}^2 \rightarrow \{\frac{M_A + M_B}{M_A M_B}\}\hat{\nabla}_{\vec{R}}^2 \qquad (29)$$

In the case of N_2, $M_A = M_B \cong 14M_p$ (i.e. 7 protons and 7 neutrons). The static potential in (28) is defined by

$$V_{static}(\vec{r}, R) = \langle \Phi^*_{N_2} | V_{e-N_2} | \Phi_{N_2} \rangle \tag{30}$$

In order to give a more realistic result, a Hara Free Electron Gas (HFEG) local exchange potential is employed and also a local polarization potential is used ∋

$$V_{static}(\vec{r}, R) \rightarrow V(\vec{r}, R) = V_{static} + V_{HFEG} + V_{pol} \tag{31}$$

The remaining potential term in (28) is the energy of N_2 as a function of R and is given by

$$\epsilon_{N_2}(R) \equiv \langle \Phi^*_{N_2} | H_{N_2} | \Phi_{N_2} \rangle \tag{32}$$

The azimuthal dependence of ψ is a constant of the motion $\Rightarrow$

$$\psi(\vec{r}, R) = e^{im\phi} \frac{s(r, \theta, R)}{rR} \tag{33}$$

Thus (28) becomes

$$\begin{aligned} \{ &- \frac{\partial^2}{\partial r^2} - \frac{1}{7(M_p/m_e)} \frac{\partial^2}{\partial R^2} \\ &- \frac{1}{r^2} [\frac{1}{sin\theta} \frac{\partial}{\partial \theta} sin\theta \frac{\partial}{\partial \theta} - \frac{m^2}{sin^2\theta}] \\ &+ \epsilon_{N_2}(R) + V(\vec{r}, R) - E \} s(r, \theta, R) = 0 \end{aligned} \tag{34}$$

Note the implicit dependence of s on $m \ni s = s^{(m)}$.

We prefer to rewrite (34) as

$$\begin{aligned} [\Delta_{\underline{r}}(m) + 2\mu \frac{d^2}{dR^2} + k^2(R)] s(\underline{r}, R) = \\ 2\overline{V}_{e-N_2}(\underline{r}, R) s(\underline{r}, R) \end{aligned} \tag{35}$$

where

$$k^2(R) = 2[E - \epsilon_{N_2}(R)] \tag{36}$$

and

$$\epsilon_{N_2}(R) = E_T^{(e)}(R) + V_{nn}(R) \tag{37}$$

where $E_T^{(e)}(R)$ is the electronic potential energy of N_2 and $V_{nn}(R)$ is the nuclear repulsion in N_2.

Also

$$\Delta_{\underline{r}}(m) \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}[\frac{\partial^2}{\partial \theta^2} + cot\theta \frac{\partial}{\partial \theta} - \frac{m^2}{sin^2\theta}] \tag{38}$$

(B) Boundary Conditions

Because we are solving an elliptic PDE, the value of s must be specified on all boundaries. Refering to Fig. 2 showing the scattering volume, there are six boundary surfaces. Because we have defined a continuum orbital which is reduced in r and R, it is clear that $s = 0$ on surfaces 2 and 4. We are also going to restrict to the Π_g scattering symmetry (this is not essential, but is done for simplicity in this first calculation), so that $s = 0$ on surfaces 1 and 6. Only surfaces 3 (large R) and 5 (large r) are not taken care of. In order to treat the boundary surface 3, we restrict to scattering energies $\ni$

$$E \leq DE \cong 9.7536 eV$$

for the potential surface of Zare for N_2. Thus $s = 0$ because $k^2(R) < 0$ and R is sufficiently large that the orbital has decayed to zero inside the potential barrier. Note that if $k^2(R) > 0$, the particle would be free on surface 3. The remaining surface is surface 5. This is the large $r = \rho_2$ surface. Here we solve (34) for a set of solutions for different l, m, and v where we define the micro-channel solutions by

$$s_{vl}^{(m)}(\rho_2, \theta, R) = P_{lm}(\theta)\phi_v(R) \tag{39}$$

Then

$$s_{vl}^{(m)}(r > \rho_1, \theta, R) =$$
$$\sum_{v\lambda} P_{\lambda m}(\theta)\phi_v(R) \tag{40}$$
$$[A_{v\lambda,vf}\hat{j}_\lambda(k_n r) + B_{v\lambda,vf}\hat{n}_\lambda(k_n r)]$$

Note that $\rho_1 < \rho_2$ and ρ_1 must be large enough that (40) is valid. The N_2 vibrational wavefunctions satisfy

$$[-\frac{1}{7(M_p/m_e)}\frac{d^2}{dR^2} + E_T^{(e)}(R)]\phi_v(R) = \epsilon_v\phi_v(R) \tag{41}$$

The solution procedure consists of
1. Solve (34) for a sufficient set of v, l, m defining the boundary conditions at $r = \rho_2$.
2. From these solutions, calculate the projections

$$s_{v'l',vl}^{(m)}(\rho_2) =$$
$$\int\int \phi_{v'}(R)P_{l'm}(\theta)s_{vl}^{(m)}(\rho_2, \theta, R)sin\theta \ d\theta \ dR \tag{42}$$

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3. Then use

$$s^{(m)}_{v'l',vl}(\rho_1 < r < \rho_2) =$$
$$[A_{v\lambda,vf}\hat{j}_\lambda(k_n r) + B_{v\lambda,vf}\hat{n}_\lambda(k_n r)] \tag{43}$$

equating (42) and (43) for two different values of r, one of which can be ρ_2, and for all relevant indices $v', l' \leq v, l$. The K matrix is then determined from

$$K_{v'l',vl} = \sum_{\nu\lambda}(A^{(-1)})_{v'l',\nu\lambda}B_{\nu\lambda,vl} \tag{44}$$

The solution for the other value of r_1 is obtained by backing the solution in from $r_2 = \rho_2$ to $r = r_1$. Then a simple 2x2 matrix inversion is required to determine the A and B matrices.

(C) Finite Differences

Applying a second order finite difference representation of the partial derivatives with respect to r, θ and R, we obtain (we only show the r derivatives)

$$\frac{\partial s(r,\theta,R)}{\partial r} \approx \frac{s_{i+1,j,k} - s_{i-1,j,k}}{2h_r} \tag{45}$$

$$\frac{\partial^2 s(r,\theta,R)}{\partial r^2} \approx \frac{s_{i+1,j,k} - 2s_{ijk} + s_{i-1,j,k}}{h_r^2} \tag{46}$$

similar expressions obtain for θ and R. The expression that is actually programmed is

$$s_{i+1,j,k} + s_{i-1,j,k} +$$
$$a^+_{ij}s_{i,j+1,k} + a^-_{ij}s_{i,j-1,k} \tag{47}$$
$$bs_{i,j,k+1} + bs_{i,j,k-1} + c_{ijk}s_{ijk} = 0$$

where

$$a^{\pm}_{ij} \equiv \frac{h_r^2}{r_i^2 h_\theta^2} \pm \frac{h_r^2 \cot\theta_j}{2r_i^2 h_\theta} \tag{48}$$

$$b \equiv \frac{2\mu h_r^2}{h_R^2} \tag{49}$$

$$c_{ijk} \equiv -2 - \frac{2h_r^2}{r_i^2 h_\theta^2} - \frac{mh_r^2}{r_i^2 \sin^2\theta_j}$$
$$- \frac{4\mu h_r^2}{h_R^2} + h_r^2 K_k^2 - 2h_r^2 V_{ijk} \tag{50}$$

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Ilustrated on the diagram is an example matrix representation of the finite difference approximation to Eq. (47) corresponding to 3 R points, 3 θ points, and 4 r points.

(D) Extension To Polyatomic Scattering

The basic theory of the PDE method has been extended to include electron scattering from polyatomic molecules in the fixed nuclei approximation. We shall neglect, in this short sketch, any mention of irreducible representations, antisymmetry.

Specifically, the fixed-nuclei amplitude can be written:

$$f(\beta_0, \Omega') = \sum D_{0m}^{(l_1')*}(\beta_0) a_{mm'}^{(l_1' l_2')} D_{m'm}^{(l_2')}(\beta_0) \qquad (51)$$
$$Y_{l_2' m_2}(\Omega')$$

The total wave function is written

$$\Psi = \sum_{\lambda\mu} \frac{1}{r} \psi_{\lambda\mu}(r, \Omega) Y_{\lambda\mu}^*(\Omega_0) \Phi_{target} \qquad (52)$$

Φ_{target} is assumed to be known in some reasonable approximation. $\Omega = (\theta, \phi)$ are the spherical angles describing the scattered particle in a body-fixed frame; Ω_0 are the angles of the incident particle (which is *not* the z-axis) in the body frame.

Substitution in the fixed-nuclei Schrödinger equation and premultiplication by

$$\langle \Phi_{target}^* \Psi_{l'm}(\Omega_0) | \qquad (53)$$

yields the desired 3d-pde

$$[-\frac{\partial^2}{\partial r^2} - \frac{1}{r^2}(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}) + \qquad (54)$$
$$V(r, \theta, \phi) - k^2]\psi_{lm}(r, \theta, \phi) = 0$$

Note: $k^2 = E - E_{target}$ and

$$V(r, \theta, \phi) = \langle \Phi_{target} V_{e-target} \Phi_{target} \rangle \qquad (55)$$

Note that V is independent of Ω_0, which is a boundary condition and not a dynamical variable; that is the key point of the fixed-nuclei approximation.

It is important to realize that for general polyatomic scattering, the potential and hence the solutions are not diagonal, neither in l nor m. These indices are useful because they define asymptotic boundary conditions; the solutions, so indexed, can be expected to converge rapidly in l (with $-l \leq m \leq l'$) for low energy scattering.

Specifically, defining individual solutions by their boundary conditions at $r = \rho$ large,

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$$\Psi \propto Y_{lm}(\Omega) \qquad (assuming\, V \to \infty) \tag{56}$$

we can project to find radial functions

$$f_{l'm',lm}(r) = \int Y_{l'm'}^*(\Omega)\psi_{lm}(r,\Omega)d\Omega \tag{57}$$

from which the $K - matrix$ can be evaluated.

The above equations apply to electron-molecule scattering in the static exchange approximation.

Thus we see that in equation (12), the integral of the continuum orbital with bound orbitals must be calculated. It has been found that a higher order algorithm is needed. This extension to an arbitrary order algorithm is in progress.
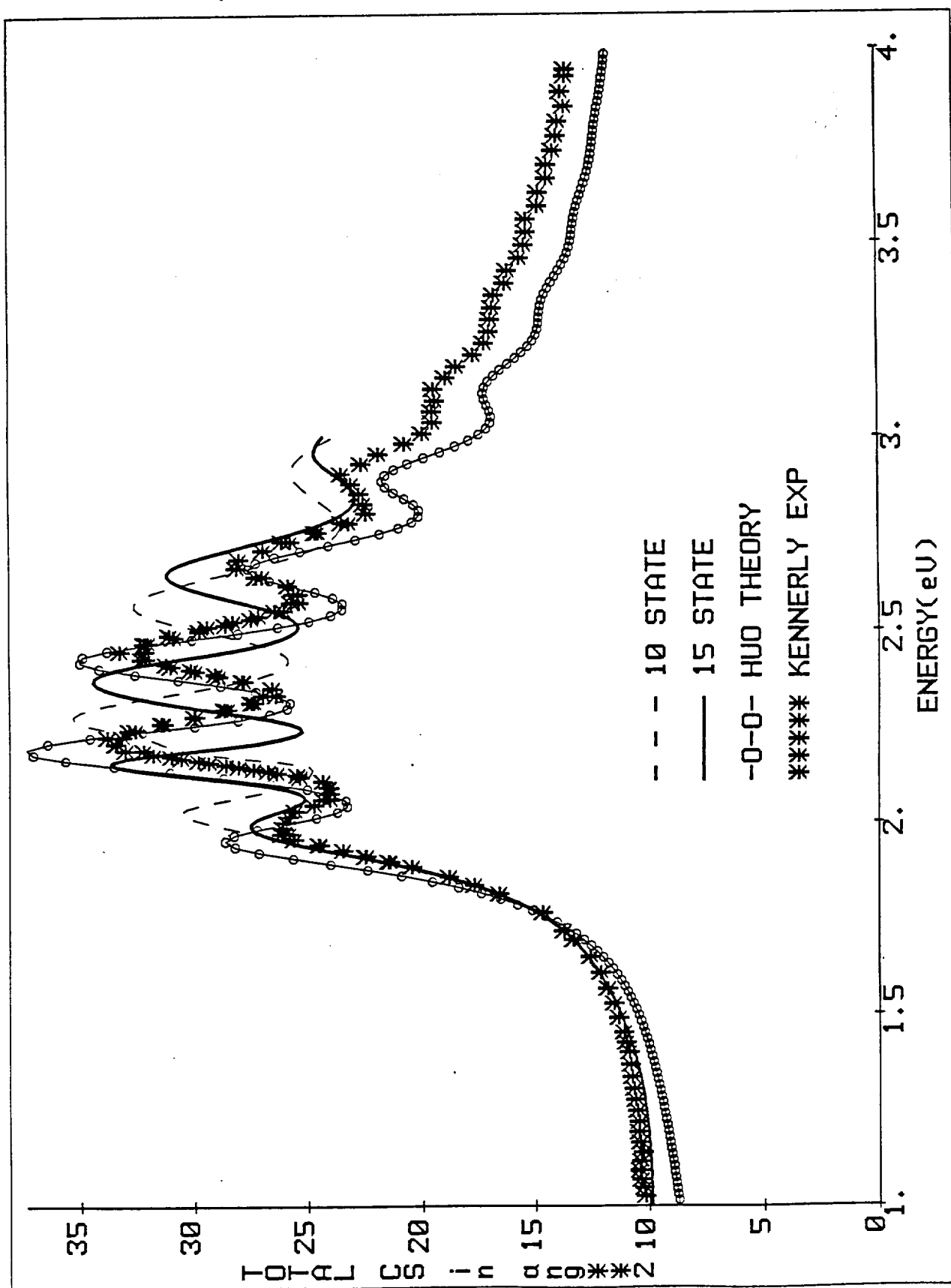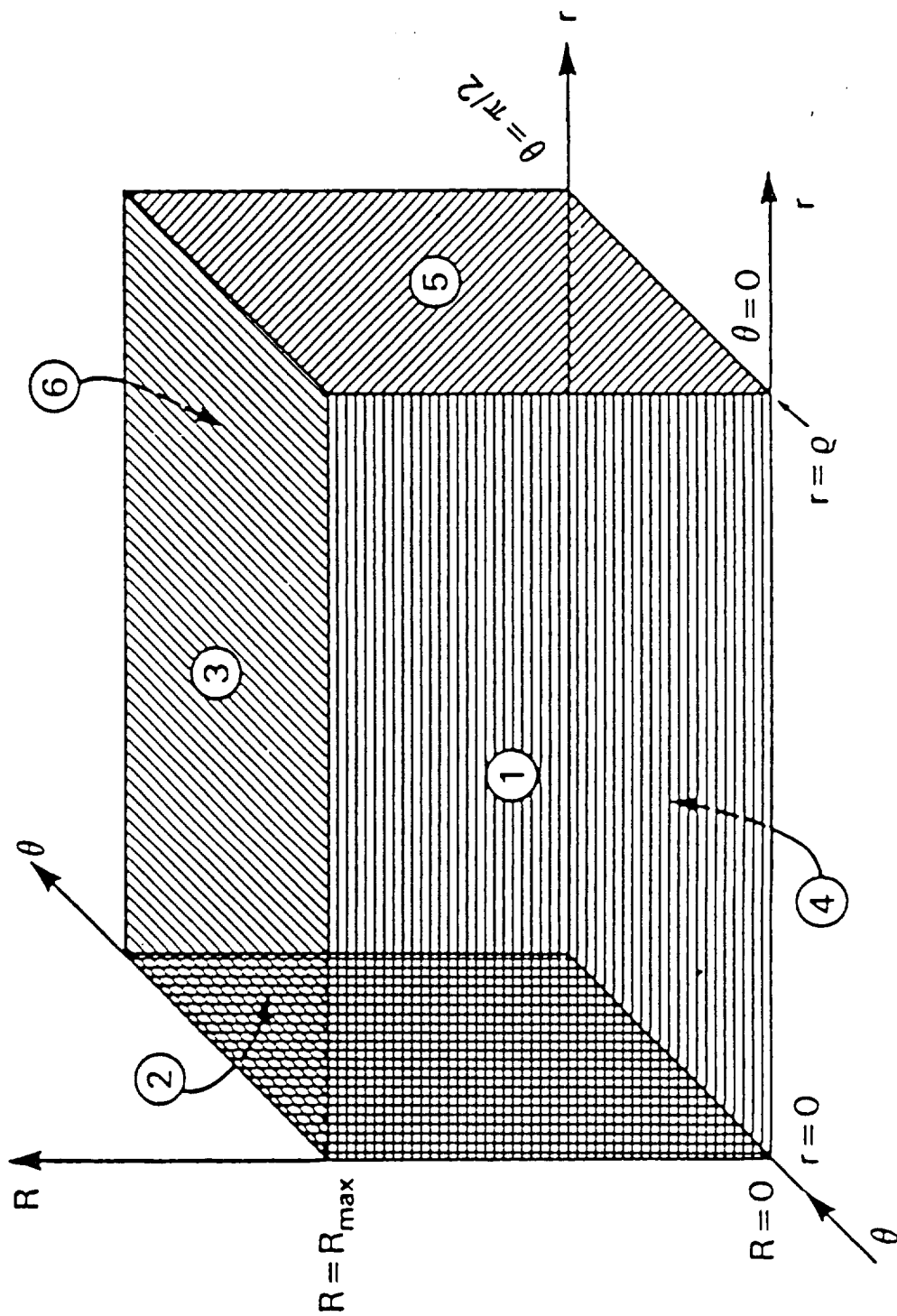
Fig. 2

ENERGY(eV)

- - - 10 STATE
—— 15 STATE
-O-O- HUO THEORY
***** KENNERLY EXP

Fig. 2

Fig. 3